Office of Naval Research Workshop on Prevention of Environmental Degradation of Advanced Materials at Temperatures above 1000°C
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Report of Session A: Environmental (Oxidation) Protection Including Advanced Coating Concepts at Temperatures Above 1000°C

1) High Temperature Coatings (1000° to 1650°C)

The recommendations in this section are concerned with reusable reentry vehicles, aircraft turbine engines and commercial-industrial turbines operating in the 1000° to 1650°C (1832° to 3000°F) range for time periods of days to weeks. The materials systems to be considered are superalloys and covalent-fiber (e.g. C, SiC, Si_3N_4) composites, with carbon, SiC, Si_3N_4, glass-ceramic and $MoSi_2$ matrices. Past work has identified two general types of viable coatings and coating combinations. These are: (1) silicon-based coatings on ceramic-matrix and carbon-carbon composites, and (2) thermal-barrier coatings (TBCs) for advanced superalloys.

The basic research issues identified for increased attention in silicon-based coating systems are: (1) studies of the effects of additives (e.g. B, Ge), moisture and oxygen pressure on oxide adherence and viscosity to provide the understanding and data necessary for effective minimization and control of sealant and scale cracking, (2) analysis and modeling necessary for developing duplex and glass coatings with optimum thermal expansion, strain tolerance and plasticity for crack management, (3) studies of realistic functionally graded coatings, which utilize gradation of coatings and/or a series of layers to control crack initiation and especially crack propagation, (4) include when possible, measurements, analyses and realistic modeling of the effects of applied stresses on coating systems, (5) electrolytic inhibition of transport through silica scales at the higher temperatures where silica is an ionic conductor.

Advances in electron-beam physical-vapor deposition (EBPVD) processing of thermal-barrier coatings for advanced superalloys have provided strain-tolerant coatings offering the advantage of increasing the operating surface temperature several hundred degrees. Recent work has indicated that TBCs with novel microstructures can further increase thermal resistance. For example, the thermal conductivity of a nanocrystalline YSZ coating is reduced 40% relative to a state-of-the-art EBPVD YSZ coating. Key fundamental studies which could lead to more thermal-efficient TBCs and higher operating surface temperatures are: (1) measuring the effects of temperature and film thicknesses on thermal conductivity, (2) developing microstructural models of the dependence of thermal conductivity on grain size and other interfaces, and (3) studying the effect of thermal exposures in

the 1200°-1500°C range on microstructural stability and thermal properties.

Another important advantage of more thermal-efficient TBCs is the catalytic reduction of NO_x emissions due to the higher gas-combustion temperatures. Basic kinetic studies of YSZ doped with selected catalytic oxides could result in new chemically-modified TBCs with even greater reductions in NO_x and other undesirable emissions.

2) Very-High Temperature Coatings (1650° to 2000°C)

Effective coatings are needed to protect carbon-carbon and carbon-SiC composites from oxidation in limited-life turbine and reusable reentry applications in the 1650° to 2000°C (3000° to 3632°F) range for periods of 10 to 50 hours. Past work has identified three types of coatings that are appropriate for the indicated temperatures and times. These are (1) silicon-based ceramics for temperatures below 1800°C (3272°F), (2) iridium-aluminum intermetallics for temperatures up to 1900°C (3452°F), and (3) hafnium and zirconium borides and carbides with SiC additions for temperatures up to 2000°C.

The silicon based materials SiC and Si_3N_4 are preferred as coatings because of their low CTEs and the low oxidation rates provided by SiO_2 scales. Previous work has shown that temperature limitations vary with coating stoichiometry and oxygen partial pressure, and that coating failure is usually due to either (1) active oxidation with SiO(g) formation or (2) SiO_2 scale disruption by CO(g) or N_2(g) release. Basic studies which can lead to improvements in the operating range and durability of these coatings are: (1) new passivation approaches to protect against active oxidation, (2) investigations to clarify the effects of scale devitrification and stress on oxidation, and (3) electrolytic inhibition of oxidation at extreme temperatures.

Iridium aluminides with compositions between IrAl and $IrAl_{2.5}$, which have been investigated recently, have the potential for providing oxidation protection to approximately 1900°C. Suggested basic investigations are: (1) studies to improve bonding with carbon-carbon and SiC substrates and (2) studies to determine the effects of silicon additions to these aluminides which can result in greatly decreased oxidation rates and extended lifetimes.

Coatings composed of the borides and carbides of zirconium or hafnium with SiC additions have been shown to have excellent short-time oxidation resistance up to 2000°C. CVD coatings composed of alternating HfC and SiC layers are an example of recent tailored microstructures which exhibit improved oxidation resistance. Suggested basic studies are the effects on oxidation rates and scale characteristics of (1) coating composition, (2) morphology and microstructure, (3) oxygen pressure and (4) stress.

The iridium aluminides and refractory borides and carbides have high CTEs relative to carbon-carbon and carbon-SiC composite substrates. Interface-modeling is needed to identify optimum interface configurations.

3) Ultra-High Temperature Coatings (2000° to 3000°C)

Reliable coatings are needed to minimize the oxidative erosion of carbon-carbon and carbon-carbide composites in single-use rocket propulsion and aerodynamic heating reentry applications at temperatures in the 2000° to 3000°C (3632° to 5432°F) range for times of several minutes. Past work has identified two general types of viable coatings and coating combinations. These are (1) refractory carbides as solid solutions or mixtures, and (2) iridium or iridium-rhenium alloys overlaid with refractory oxides. Prominent coating-performance issues are (1) oxygen permeation of intact coatings, (2) coating damage and spallation, and (3) coating erosion. The most fruitful basic oxidation, composition-phase constitution and interface-design studies needed to address these issues for the two types of coatings are summarized below.

Recent work has shown that HfC forms coherent and adherent HfO_2 scales at temperatures over 2000°C and is an appropriate coating material for ultra-high temperature applications. Fundamental issues to be investigated are (1) the effects of carbide stoichiometry and oxygen pressure on oxidation rate and scale characteristics, (2) how additions of SiC and TaC (which are thought from past empirical work to enhance oxidation resistance) change the HfC oxidation rate and oxidation product characteristics, (3) the oxidation of HfC-ZrC solid solutions, which could be important for reduced cost and weight, and (4) the viscosity and wetting behavior of liquid oxidation products that form at the very highest temperatures and are susceptible to flow erosion.

Combining an iridium inner coating to provide very low oxygen permeation and an outer HfO_2 layer to prevent oxidative erosion of the iridium has the potential to provide greatly improved protection compared to the refractory carbide coatings. Past work has shown that iridium bonds poorly to carbon. An approach to solving this problem is to alloy iridium with rhenium to take advantage of the high carbon solubility of rhenium. Important areas for investigation here are (1) a general definition of the Ir-Re-C system, (2) the behavior of C-Ir, Re diffusion couples in terms of phase formation and bonding, and (3) the oxygen permeability of Ir-Re alloys.

Both types of coatings discussed above have significant CTE mismatches with the carbon-fiber reinforced substrates. Therefore micromechanical modeling and coating-substrate interface design studies are needed to identify optimum ways of configuring the interfaces.

Report of Session B: Environmental Effects on Stability of Ceramic-Matrix-Composite (CMC) Interfaces and Resultant Mechanical Behavior

General Summary

The most pressing needs and impacts are in the applications of CMCs for gas-turbine engine structures operating in the range of 1000° to 1400°C. This temperature range covers most applications in the combustor, turbine, and nozzle section of both military and commercial engines. While more advanced applications in the future might require CMCs that would have to perform at temperatures over 1400°C, the current problems must be solved first or there may never be any long term interest in CMCs.

The most critical issue facing the utilization of CMCs in these applications is the effect of the environment on the fiber/matrix interfacial characteristics of the composites, with the ingress of environment occuring primarily due to matrix cracking under stress. Thus, the basic research priority must be focused on how to design and characterize (as well as fabricate) an environmentally stable interface while retaining the relatively weak interfacial bonding necessary for matrix crack deflection and thus toughening of the composite. It was decided that three focus areas should be prioritized: (1) optimized fiber coatings or other interface concepts that meet the above criteria; (2) optimized matrices that can limit crack propagation to the fiber/matrix interface through either crack blunting, increasing stress required to form cracks, or porosity minimization in those matrices that contain inherent porosity; and (3) a test protocol development that would include testing and characterization of the fibers, fiber coatings and resultant composites in a well coordinated manner that would emphasize university/national laboratory/industry cooperative efforts.

Priority needs in the fiber coating area were decided to be in three areas: (1) boron nitride (BN) and/or other boron containing compounds, (2) new fiber coating concepts, and (3) the possibility of in-situ formed fiber coatings. Boron nitride was selected because it is being used widely and has shown promise for use in CMCs up to 1100° to 1200°C, but has not been investigated thoroughly as far as understanding the effects of BN microstructure, thermal stability, interaction with fibers and matrices, and the effect of moisture and other environments. This also holds for other boron-based coatings, i.e. B-C mixtures. Other fiber coatings such as layered structures, porous coatings, and fugitive interfaces are being investigated under current programs, primarily the HSCT/EPM program, but are not well understood in the same areas mentioned above for BN coatings.

In-situ formed interfaces would go a long way in reducing the cost and fabrication complexity of CVD coatings on fibers, and have been studied for carbon interfaces on Nicalon SiC fibers in glass matrix composites, and BN interfaces on Nextel 312 aluminosilicate fibers in polymer pyrolyzed composites by nitriding the B containing Nextel fibers at high temperatures prior to composite fabrication, but the composites made with these interfaces have been found to lack either oxidative or thermal stability. Perhaps other fibers and/or matrices could be deliberately doped such that suitable interfaces could form at high temperatures.

Matrix engineering deals with crack blunting via seal coatings or dopants (fillers) to the matrix, inhibiting the formation of matrix cracks under stress by toughening the matrix with additions or microstructural optimization that would increase the matrix microcracking (or proportional limit) stress, or by minimizing the porosity that allows the environment to invade the composite in those composites that are inherently porous (PIP, CVI, sol-gel). Hybrid processing is one means that is under study to limit the porosity, and signifies the combination of say PIP and CVI processing, to fill in the open porosity that exists in either of these methods alone.

The priority need for test protocol refers to the way that new conceptual fiber coatings or interface and matrix microstructural optimizations are characterized. In particular, the mechanisms that are operable in these new concepts in composites that are being stressed, either staticly or cyclicly, must be defined. Too often, the detailed microstructural characterization that is required to assess the changes that are occurring in the composites at high temperatures under stress in a variety of environments is lacking. A coordinated joint effort between the fiber coater, the composite fabricator, the composite tester, and the composite micro-analytical characterizer is recommended. Often, this can be a cooperative effort between a university(s) and one or two industrial partners. This is sometimes difficult to structure in that many industries consider their technology proprietary, and cannot sign agreements with university researchers who need to publish their results. However, it can be accomplished in many cases and needs to be encouraged so that new and promising advances in the CMC area receive the in-depth analysis required, but also be subjected to the fabrication and scale-up environment that only industry can offer.

The subject of environmental degradation of CMCs is a complicated area in which new, revolutionary ideas and significant advances in the state-of-the-art are major challenges. The major research issues and needs idintified in session B are outlined on the following four pages.

Environmental Effects on Stability of CMC Interfaces and Resultant Mechanical Behavior

• Emphasis on gas turbine structural applications in the 1000° to 1400°C temperature range.

• Critical issue is effect of environment (oxidation, moisture, temperature, corrosion) on the interface chemistry, structure, bonding, and fiber strength due to matrix cracking under stress.

• Research should be selected in light of prior and current interface and fiber coatings studies, and should focus on CMCs of practical interest.

•Research priority is the fiber/matrix interfacial design and characterization for environmental stability and debond criteria.

• Priority Needs
  - •Optimized fiber coatings/interface concepts
  - •Matrix engineering for crack limitation and blunting
  - •Test protocol

PRIORITY NEEDS-
OPTIMIZED FIBER COATINGS/
INTERFACE CONCEPTS

- BN and/or boron containing compounds/multiphase systems

    - Understanding chemistry, microstructure, processing/property relationships

    - Limiting life aspects: oxidation, hydration, thermal stability, fiber/coating/matrix stability, envelope of use

    - Environments of practical interest (external, internal)

- Fiber coating concept development
    - Layered, porous, fugitive, doped C, new compounds, etc.
    - Affordable and applicable for practical CMC

- In-situ formed interfaces

- Modeling and verification

- Priority CMC systems containing SiC fibers, SiC containing overcoats and/or matrices

PRIORITY NEEDS-
MATRIX ENGINEERING

- Crack blunting
  - Seal blunting (boron containing glass formers)
  - Fillers (inert and reactive)
  - Modeling and verification

- Limit crack formation (increase the proportion limit)
  - Matrix additives and microstructures to increase toughness

- Porosity minimization
  - Fiber geometry
  - Hybrid processing
  - Fillers

PRIORITY NEEDS-
TEST PROTOCOL FOR NEW INTERFACE AND COATING CONCEPTS

Proof of Concept and Mechanisms (Porous, Layered, Fugitive, Doped)

- Coating/Fiber Tests
    - Fiber coating processability
        - UTS, SEM, TEM, Auger
    - Mechanical, physical, chemical interactions

- Matrix/Coating/Fiber composite fabrication
    - Room temperature testing
    - Fracture analysis (push and tensile tests)
    - Microstructural evaluation

- Composite testing
    - Elevated and intermediate temperatures
    - Static and cyclic fatigue (oxidative and inert environments)
    - Creep
    - Microstructural evaluation

- Industry/national laboratory/university coordination recommended

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